Selective Transport of Alkali Metal Ions Across Black Lipid Membranes (BLM) Composed of Ionophilic Amphiphiles[1]

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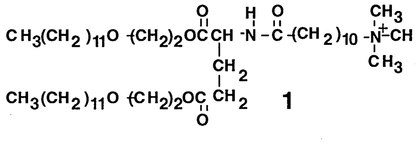
Transport of alkali-ions across black lipid membranes (BLM) formed from cationic and anionic, double-chain amphiphiles was characterized by the charge pulse relaxation technique. Amphiphiles containing an ether linkage in the alkyl tail portion displayed enhanced transport rates for sodium and potassium ions, while such selectivity is not observed for the related amphiphile without the ether linkage.

Selective ion transport phenomena across bilayer membranes is one of the essential features of cellular functions. Planar bilayer membranes (BLM's) represent one of the simplified experimental systems for elucidating membrane transport phenomena,[2] and ion transport has been facilitated in the presence of ionophores[2,3] or channel-forming molecules.[2,4-11] In case of the latter molecules, polyoxyalkyl chains are often employed as hydrophilic membrane-spanning moieties.[7-11] We have shown that synthetic amphiphiles form stable BLM's, in which transport of hydrophobic ions are affected by polyioncomplex formation[12] as well as by polymerization.[13] In the present study, BLM's which have an ether linkage in the alkyl tail portion are found to display selective ion-transport, without adding specialized transport molecules. We have reported that the presence of ether oxygen in the alkyl tail *e.g.*, **1** and **2**, imparted the bilayer with flexibility without losing the regular side-chain alignment.[14] This advantage provided an indispensable molecular design for polymerizable bilayers,[13] matrix bilayers for protein assembly,[15] and, more recently, complementary hydrogen bond-mediated bilayers.[16]

BLM's of **1-3** were prepared by brushing a hole (diameter ; 0.85 mm) in a Teflon plate that was immersed in 0.1 M aqueous NaCl, KCl, CsCl, and LiCl at 25 ℃. The amphiphiles were dissolved in mixtures of decane and $CHCl_3$ (4 : 1 by volume). The electrical properties of BLM's were measured as described previously.[12,13]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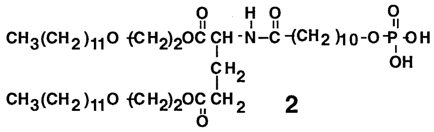
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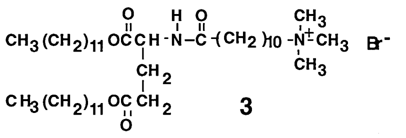
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The membrane capacitance (C_M) obtained for BLM's **1-3** in the presence of various alkali ions are summarized in Figure 1. Ammonium amphiphile **3** was used as a reference. It is apparent that C_M values are dependent on the amphiphilic structure, while they are not affected by the alkali- ion species. C_M is inversely proportional to bilayer thickness,[2,13] and the observed C_M values are in the range of those reported for synthetic BLM's.[12,13]

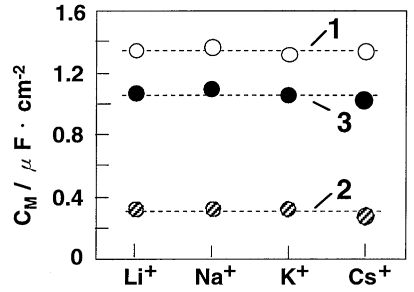

Figure 1. Dependence of C_M on alkali-ion species.

Permeation of ions across BLM's would proceed via the following three steps[2,12] : (1) adsorption of the ion from the aqueous phase to the membrane-solution interface; (2) translocation to the opposite site ; and (3) desorption into the aqueous solution. The rate constant of translocation , k_i, and the relative rate constant of adsorption and desorption, $\beta = k_{in}/k_{out}$, can be evaluated directly by the charge-pulse technique.[2,12-13]

Figures 2 and 3 display the dependence of β and k_i values on alkali-ion species. It is known that lipid membranes are extremely impermeable to small ions,[2] and as expected, the saturated-chain amphiphile **3** showed nearly constant β and small k_i values with respect to the change in alkali-ion species. The β value is smaller for the phosphate amphiphile **2** than those of cationic amphiphiles **1**, **3**. This can be ascribed to the electrostatic binding of alkaline ions at the bilayer surface and hydrogen bond network among phosphate head groups, that slower the rate of dynamic desorption / adsorption process after the applied charge pulse. Surprisingly, ether-linkage-doped amphiphiles **1** and **2** showed enhanced β values for Na$^+$, compared with the other cations (Figure 2). As these two bilayers components possess oppositely charged head groups, it is the aligned ether linkages that have effectively increased affinity for Na$^+$ ion. In the case of ammonium bilayer **1**, a slight increase in β is also observed for K$^+$ ion .

Figure 3 displays the influence of the amphiphilic structure on the translocation rate constant (k_i). Bilayers **1** and **2** possess larger k_i value for Na$^+$ and K$^+$ ions than Li$^+$ and Cs$^+$ ions.
As such selectivity is not observed for **3**, the enhanced translocation rates are probably derived from the presence of

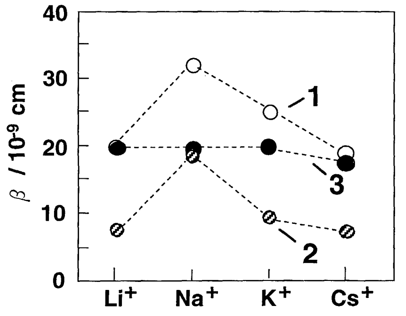

Figure 2. Dependence of β on alkali-ion species.

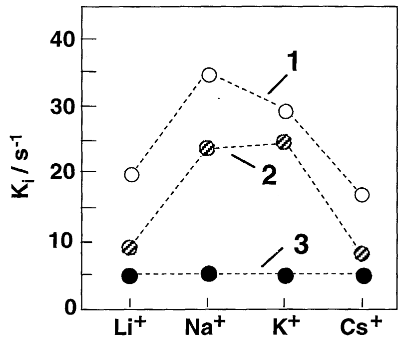

Figure 3. Dependence of k_i on alkali-ion species.

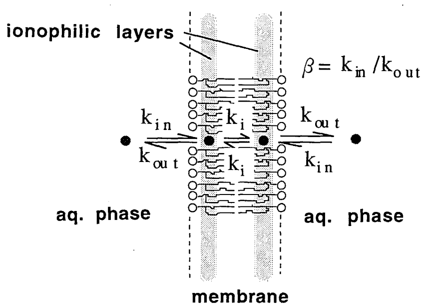

Figure 4. Schematic illustration for transport of alkali-ions across ionophilic BLM.

"ionophilic" layers consisting of two-dimensionally organized ether linkages in the interior of bilayers (Figure 4).[17] It is conceivable that the adjacent ester and amide linkages of the glutamate unit also contribute to the ionophilic layers. Within the series of alkali-metal ions, Li^+ is most strongly hydrated and thus its adsorption to the membrane surfaces from solution interface may not be facilitated. On the other hand, adsorption and successive translocation is not facilitated for Cs^+ ion, since its large size necessitates to create space between the aligned amphiphiles.

In conclusion, we demonstrated that BLM's composed of ether linkage containing glutamate amphiphiles display selective alkali-ion transport properties in the absence of carrier or channel molecules. Though the origin of selective transport is not well known at the molecular level, introduction of one ether linkage in the chain portion leads to an ionophilic interior in the bilayer. This finding provides a basis for designing new membrane transport systems.

References and Notes

1 Contribution No.1025 from Department of Chemical Science and Technology.
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17 Gel-to-liquid crystal phase transition temperatures (Tc) of aqueous bilayers **1** and **3** are almost identical (**1** ; 35 ℃, **3** ; 34 ℃), and thus the observed selective cation translocation is not associated with the difference in membrane fluidity.